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Long-Term Cathodoluminescent Characterization of Thin-Film Oxide Phosphors in a Wide Range of Electron Excitation Densities.

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ABSTRACT

Long-term processes of cathodoluminescence degradation of thin film phosphors Zn_2SiO_4:Ti and Zn_2GeO_4:Mn were investigated in a wide range of e-beam energies, current and power densities. The time dependencies describing decreasing of emission intensity have been found. At high-level densities of e-beam irradiation the specific behavior of long-term degradation processes was observed, which is characteristic with rapid degradation at initial stage and slow consequent decrease of intensity. The most probable mechanisms responsible for long-term processes of degradation in investigated phosphors are proposed.

INTRODUCTION

Thin film oxide phosphors are prospective for low-voltage field-emission display applications due to their appropriate color coordinates, high efficiency [1,2], and possibility of creation of increased conductivity[3] in them. Long-term stability of phosphors is also very important for practical applications, especially for development of field-emission displays with low-voltage excitation (less than 3 keV) where excitation takes place in near surface layer which is extremely sensitive to degradartion. The degradation processes were intensively studied in a series of works [2, 4-10]. The two main mechanisms have been found to be responsible for decreasing of cathodoluminescence (CL) intensity: irreversible one, caused by physical and chemical reactions, and the reversible one (thermal quenching), caused by thermal heating with electron beam. Several regularities describing CL degradation behavior have been found in [5-8]. Some new regularities describing long-term behavior of series of thin film oxide phosphors have been found by authors of present work [2,10]. Results of more detailed studies of degradation processes in a wide range of excitation energies, e-beam currents and excitation intensities for the case of phosphors with charged luminescent centers, which are the most sensitive ones to the processes of thermally diffusion quenching are presented in current work.

EXPERIMENTAL

Thin films were deposited by modified rf-magnetron method [11] with consequent high-temperature recrystallization at 650-1050°C. CL was measured at continuous electron excitation with the energy of 1-3.5 keV, e-beam currents of 20-200 μA and beam diameter of 3 mm which corresponds to e-beam current densities of 0.28 - 2.8 mA/cm^2 and power densities from 0.1 to 20 W/cm^2. This mode of measurements during 8 hours corresponds to approximately 1500 hours of excitation of conventional 21-inch kinescope at 25 kV and 1 mA (assuming equal deposited charges per square cm. during irradiation). Measurements were made on the laboratory-made prototype of CRT with thin film phosphor samples mounted on a faceplate. Two methods were used for avoiding possible errors caused by nonstability of e-beam and photoreceiver: periodical deflection of e-beam to the non-irradiated area and simultaneous measurement of e-beam current and energy with subsequent correction of intensity data. Both methods showed good stability and accuracy in long-term measurements of CL intensity.

RESULTS AND DISCUSSION

It was found that at power densities less than 0.5 W/cm^2 most of oxide thin films phosphors did not show substantial decrease of CL intensity within the accuracy of measurements (3-5%). The decrease of CL intensity was observed at power densities greater than 1 W/cm^2 and is in a good agreement with dependency

$$(Io/I - 1) = K \cdot t^{1/2} \qquad (1)$$

which describes thermal diffusion process [10] of long-term degradation of CL intensity.

At the same time, at higher power densities of e-beam in the range of 1-20 W/cm^2 and various current densities and energies, Zn_2SiO_4:Ti phosphors showed distinctive behavior under long-term irradiation which is revealed in two-stage long-term dependency.

In the case of low excitation energies (< 2 keV) dependence (1) for Zn_2SiO_4:Ti films is linear (figure 1), and quenching (degradation) coefficient K increases from 0.01 to 0.1 with increasing of current density from 0.28 to 2.8 mA/cm^2.

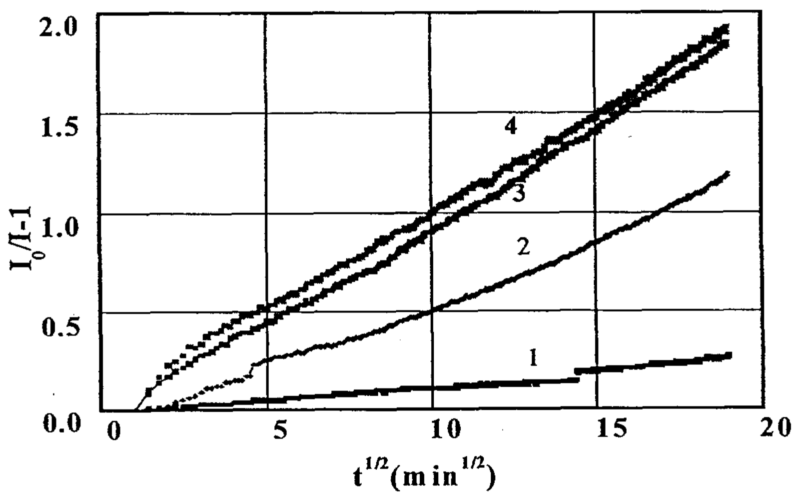

Figure 1. (I_0/I -1) vs. $t^{1/2}$ (min$^{1/2}$) plot of CL intensity of thin-films Zn_2SiO_4:Ti at 2keV and 0.71 mA/cm^2 (1), 1.42 mA/cm^2 (2), 2.12 mA/cm^2(3), 2.83 mA/cm^2(4).

At higher power densities or e-beam excitation energies (E > 2.5 keV) dependence (1) reveals in a different manner. It becomes two-stage one with a rapid decrease at initial stage with $K = 0.2$-0.4, and relatively flat region with $K = 0.01$ - 0.06 during consequent long-term period irradiation dose (figure 2). The rate of decreasing at initial stage increases with increasing of e-beam power density and is accompanied by relative decreasing of degradation rate during the final stage. The value of maximal decrease ($Io/I - 1$) at current density of 2.1 mA/cm^2 changes from 1.85 at 2 keV to 1.45 at 3.5 keV.

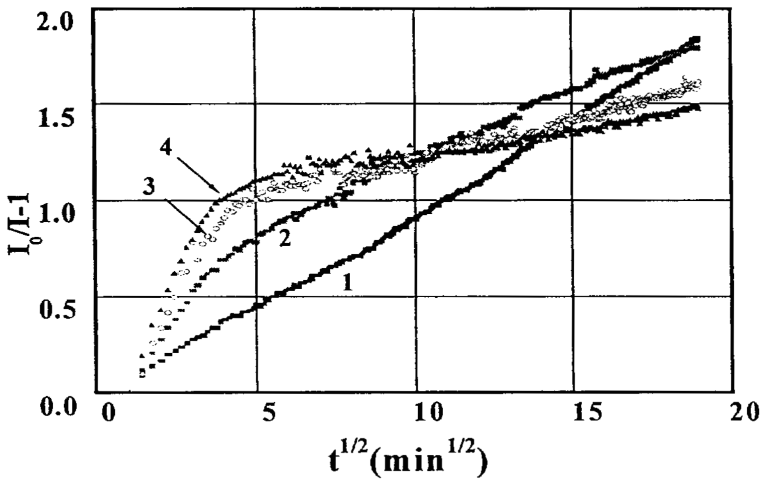

Figure 2. (I_0/I -1) vs. $t^{1/2}$ ($min^{1/2}$) plot of CL intensity of thin-films Zn_2SiO_4:Ti at 2.1 mA/cm^2 and 2 keV (1), 2.5 keV (2), 3 keV (3), 3.5 keV (4).

In the case of Zn_2GeO_4:Mn thin films the linear behavior of dependence (1) is observed at current densities not greater than 0.28 mA/cm^2 and excitation energies of 1.5-2 keV (figure 3).

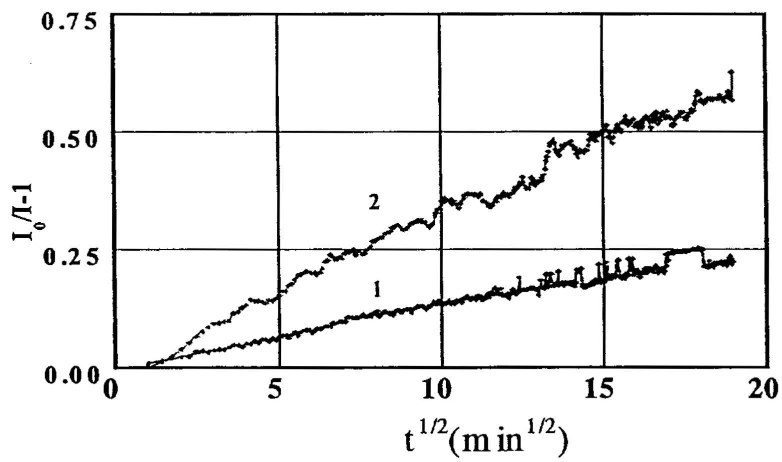

Figure 3. (I_0/I -1) vs. $t^{1/2}$ ($min^{1/2}$) plot of CL intensity of thin-films Zn_2GeO_4:Mn at 0.28 mA/cm^2

and 1.5 keV (1); 2. keV (2).

At higher current densities it becomes two-stage (figure 4). At e-beam energy of 1 keV the value of maximal decreasing ($Io/I - 1$) in Zn_2GeO_4:Mn thin films is 0.25, 0.35 and 0.70 at current densities 0.7, 1.4 and 2.1 mA/cm^2, correspondently, and after the region with rapid decrease the stabilization of intensity or even its partial increasing (buildup) is observed. At energies higher than 1.5 keV such stabilization of intensity was not observed.

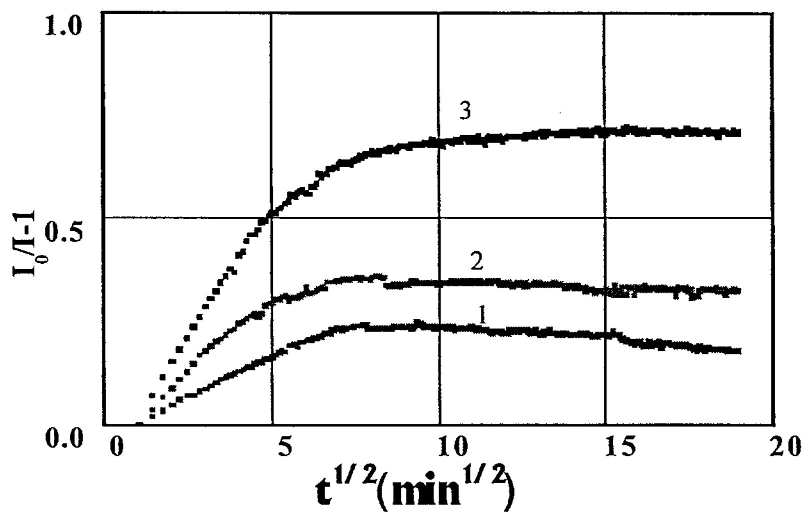

Figure 4. (I_0/I -1) vs. $t^{1/2}$ ($min^{1/2}$) plot of CL intensity of thin-films Zn_2GeO_4:Mn at 1 keV and 0.71 mA/cm^2(1), 1.42 mA/cm^2 (2), 2.12 mA/cm^2 (3).

As can be seen from the results obtained, the long-term dependencies of CL of Zn_2GeO_4:Mn and Zn_2SiO_4:Ti thin film phosphors show both similar and different behavior. The common feature for both Zn_2GeO_4:Mn and Zn_2SiO_4:Ti films is the existence of the two types of long-term dependencies:

type 1 – with linear dependency, characteristic for the range of low current densities and e-beam energies;

type 2 – two-stage long-term dependency with rapid degradation at initial stage.

The difference in long-term behavior of Zn_2GeO_4:Mn and Zn_2SiO_4:Ti thin films is that in the case of Zn_2GeO_4:Mn type 1 is limited by lower currents and energies (0.28 mA/cm^2, 1.5-2 keV) compared to Zn_2SiO_4:Ti films (0.28-2.8 mA/cm^2, 2 keV).

Coming from basic analysis of phenomena in solids and phosphors one may consider degradation to be caused by the following main processes:

- temperature quenching of luminescence centers dependent only from the temperature of a sample (power or current density);
- external quenching of luminescence due to generation of free carriers trapped by trap centers; this component also depends on nonuniformity of electron distribution in the sample, their space diffusion (drift), and trapping parameters;

- generation of defects under electron bombardment which behave as the centers of nonradiative recombination both in the volume or at the surface of phosphor;
- surface reactions (this process may be considered as special case of generation of nonradiative recombination centers on the phosphor's surface).

On the basis of obtained results the most probable mechanisms responsible for long-term stability may be:

- intrinsic temperature quenching, which is indicated by increasing of degradation coefficient with increasing of current density at the same energy of excitation;
- generation of nonradiative recombination centers in near-surface area, which is indicated by increasing of degradation rate at higher excitation energies;

Let's discuss the possibility of mechanism of nonradiative recombination centers generation. The probability of impact mechanism of defects generation at investigated e-beam energies (< 4 keV) is small because such energies are much less than defect generation threshold. However, the defects may be generated by means of before-threshold mechanisms as well. In fact, several mechanisms of defects generation at before-threshold energy levels are known: multiple ionization [12] , decomposition of self-trapped holes [13], radiation-enhanced reactions [14]. Indeed, these mechanisms have been found in series of materials [15, 16], and in particular under electron excitation [17].

When nonradiative recombination centers are generated in near-surface region, the process of diffusion of free carriers generated in volume to nonradiative recombination centers, as well as the process of radiation-enhanced diffusion of defects take place, and degradation of CL intensity is proportional to $t^{1/2}$ [15]. Stabilization of luminescence degradation observed in Zn_2GeO_4:Mn can be explained as attaining equilibrium between generation of nonradiative recombination centers and their annealing.

Existence of the rapid stage of defects generation in Zn_2GeO_4:Mn at lower currents compared to Zn_2SiO_4:Ti correlates with the fact that temperature of Zn_2GeO_4:Mn thin films formation (crystallization) is lower than that of Zn_2SiO_4:Ti.

CONCLUSIONS

It was found that at power densities less than 0.5 W/cm^2 most of oxide thin film phosphors do not show substantial decreasing of CL intensity. Decreasing of CL intensity was observed at e-beam power energies higher than 1 W/cm^2 and is in a good agreement with dependency $(Io/I - 1) = K \cdot t^{1/2}$ which describes thermal diffusion process of long-term decreasing of CL intensity.

At higher densities of e-beam irradiation energies in the range of 1 - 20 W/cm^2 and various current or power densities the specific behavior of long-term degradation processes in Zn_2SiO_4:Ti and Zn_2GeO_4:Mn was found, which reveals in rapid degradation at initial stage and slow consequent decrease of intensity.

The most probable mechanisms responsible for long-term processes of degradation in investigated phosphors, which are caused by internal thermal quenching due to heating with e-beam as well as generation of nonradiative recombination centers in near-surface area are proposed.

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REFERENCES

1. V. Bondar, M. Grytsiv, A. Groodzinsky, M. Vasyliv, A. Chakhovskoi, C. Hunt, M. Malinowsky, and T. Felter, J. Electrochem.Soc. **144,** 704 (1997).
2. V. Bondar, Materials Science and Engineering B. **69,** 505 (2000).
3. V. Bondar, Materials Science and Engineering B. **70**, 510 (2000).
4. A. Pfanhl, Bell. System. Technolog. **42,** 181 (1963).
5. Shmulovich Joseph, Information Display **3**, 17 (1989).
6. H. Widdel, and D. Post, *Color in Electronic Displays*, Plenium Press, NY 1992, p. 242.
7. T. Trottier, V. Krishnamoorthy, X. M. Zhang, R. Petersen, P. Holloway. *Proc. The Third International Conference on the Science and Technology of Display Phosphors*. Huntington Beach, CA. Nov. 3-5, 1979, pp. 321-324.
8. C. H. Seager, K. R. Zvadil, D. R. Talant, W. L. Warren. *Proc. The Third International Conference on the Science and Technology of Display Phosphors*. Huntington Beach, CA. Nov. 3-5, 1979, pp. 325-326.
9. R. L. Donofrio, *Proc. Electrochemical Society*, May, 1981, pp. 381-382
10. V. Bondar, S. Popovich, Yu. Dubov, T. Felter. *Proc. The Fifth International Conference on the Science and Technology of Display Phosphors*. San Diego, CA. Nov. 8-10, 1999, pp. 329-332.
11. V. Bondar and M. Vasyliv, Ukrainian patent No. 18151 A, 01.07.97.
12. M. I. Klinger, V. V. Emtsev, T. V. Mashovets, S. M. Ryvkin, N. A. Vitovskii, Radiation Effects **56**, 229 (1981).
13. H. N. Hersh, J. Electrochem. Soc. **118**, 144C (1971).
14. D. V. Lang, Ann. Rev. Mater. Sci. **12**, 377 (1982).
15. V. L. Vinnetskii, E. E. Yaskovets, E. V. Kelman, in *Physical processes in crystal with defects*, (Institute of Physics of Ukraine Academic Science Publishers, Kiev, 1972), p. 122 (in Russian).
16. J. Klaer, D. Braugnig, F. Wulf, *Second European Conference on Radiation and its effects on Components amd System*, Saint-Malo, France, Sept. 13-16, 1993, pp.146-153.
17. G. A. Scoggan, T. P. Ma, J. Appl. Phys. **52**, 6231 (1981).